Preparation of Ge – Sb – S – I glass system via volatile iodides

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A description of the Ge – Sb – S – I glass system preparation method by interaction of germanium iodide (IV) and antimony iodide (III) with sulfur melt is given. The prepared samples were investigated by the methods of X-ray spectral microanalysis, differential scanning calorimetry, infra-red spectroscopy, Raman spectroscopy, laser mass spectrometry. The content of silicon impurity was 1–2 ppm wt., of metals – not more than 0.5 ppm wt. The glasses are characterized by high transparency in 2–10 μm spectral range.

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1. Introduction

Chalcogenide and chalcohalide glasses are traditionally produced by melting of simple substances in evacuated quartz ampoule with subsequent cooling of the melt down to vitreous state [1]. The maximum temperatures for production of glass-forming melt on the basis of germanium compounds are 800–950^{o}C and duration of the process varies from several hours to several days depending upon composition and mass of glass. A prolonged residence time of the glass-forming melt at elevated temperatures assists the entry of impurities from apparatus material into the melt which degrades the target properties of glasses and limits their application in infra-red optics.

Chalcoiodide glasses with high content of iodine can be prepared by melting of the charge at lower temperatures [1]. Glasses, enriched with iodine, are thermally instable, and emit volatile iodides and molecular iodine at low heating. It leads to the change in their composition, and, consequently, in the target properties. Iodine in amount of up to 15 at.% increases the glass-forming ability of the melt, its homogeneity, solubility of rare-earth elements and shifts the transmission edge of glasses into long-wavelength range [2 – 4]. In actual practice it is expedient to develop a method for preparation of glasses with low concentration of iodine at low temperatures.

The goal of the present work is to prepare the Ge – Sb – S – I glass system with the content of iodine not more than 15 at.% by interaction of germanium iodide (IV) and antimony iodide (III) with the sulfur melt at temperatures not more than 650^{o}C and to investigate of their properties. According to literature data [5], exposure of the melt of chalcogenide glass to higher temperatures assists the entry of impurities from the walls of quartz ampoule into the melt.

The use of the iodides of p-elements as precursors in synthesis of chalcogenide glasses is attractive due to their high volatility and lower melting temperature as compared with corresponding simple substances ($t_{melt.}$(Ge) = 938ºC, $t_{melt.}$(GeI_4) = 146ºC, $t_{melt.}$(Sb) = 631ºC, $t_{melt.}$(SbI_3) = 171ºC). Realization of this approach can be impeded by low conversion degree from iodides into chalcogenides. Thermodynamic analysis of GeI_4 – S system by the method of equilibrium constants using the experimental data on saturated vapor pressure, obtained by tensiometric method [6], proves that the conversion degree of germanium tetraiodide into germanium disulfide by reaction

$$GeI_4 + 2S \leftrightarrow GeS_2 + 2I_2 \qquad (1)$$

under equilibrium conditions at 500ºC does not exceed 27%. At the same time the reactor pressure attains 7 atm. It follows from this fact that the preparation of glass-forming melt of Ge – Sb – S – I system with the content of iodine less than 15 at.% during interaction of germanium iodide (IV) and antimony iodide (III) with sulfur melt under equilibrium conditions is impossible.

Preparation of the melt with low content of iodine and the given ratio of macro-components is possible while shifting the equilibrium of reaction (1) to formation of the products by selective removal of iodine from reactor. This process is assisted by sufficiently high values for ideal separating coefficients in $GeI_4 – I_2$, $S – I_2$ systems equal to 21 and 150, respectively, at 300^{0}C. Synthesis of the glass-forming melt during selective removal of iodine should be conducted in apparatus with mass transfer section.

2. Experimental

The iodides of germanium (IV) and antimony (III) (99.98%), subjected to double sublimation, and sulfur (99.999%), purified additionally by distillation in vacuum, were used for preparation of glasses. The used quartz ampoules were sequentially rinsed with mixture of hydrochloric and nitric acids, hydrofluoric acid and distilled water, and then were annealed in the tube muffle furnace at 800^{o}C for 12 hours.

A scheme of the set-up for preparation of the glass-forming melt, made from quartz glass, is shown in Fig.1. Chemical interaction of charge components was carried out in reactor 7 under heating. The escaping iodine vapors together with vapors of volatile iodides ascended through mass-transfer section 9 where separation took place. Iodine, as a low-boiling component, concentrated in the upper part of mass-transfer section and was collected in receiver 10. Vapors of high-boiling iodides condensed in the bottom part of separating section and drained down into the melt. It provided the selective removal of iodine from the glass-forming melt with simultaneous retention of other macro-components in the melt. Iodine was periodically extracted in the temperature range 300–650^{o}C. Rings from quartz glass with height and diameter of 6 mm were used as filling.

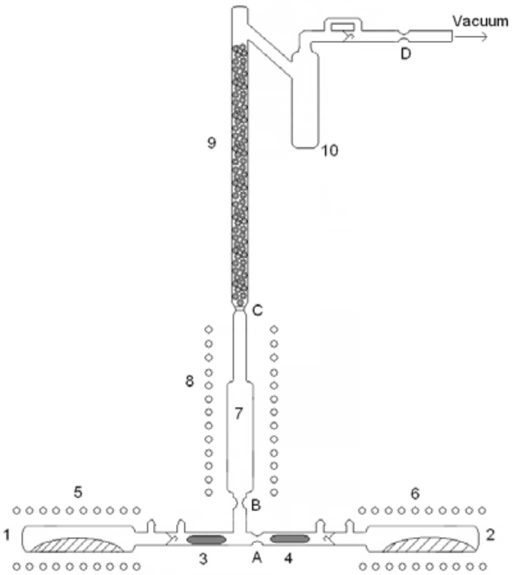

Fig.1. Set-up for glass production: 1, 2 – loading ampoules; 3, 4 – magnetic hammer-breaker; 5, 6, 8 – resistance heating furnaces; 7 – reactor; 9 – mass-transfer section; 10 – iodine receiver.

The glass-forming melt was prepared in three modes: in system open to air environment; in environment of high-pure argon; in vacuum. In the first case the charge was loaded into reactor via glass funnel, and then the mass-transfer section was filled with packing. Reactor was placed into vertical furnace and was heated up to 300^{o}C. Intensively escaping iodine vapors were condensed in receiver 10. Then the reactor temperature was increased by 30–50ºC and iodine sampling was continued. The maximum temperature of synthesis was 650ºC with duration of 8 hours. After synthesis the reactor was cooled in the mode of the switched-off furnace down to 450ºC, the melt was annealed in air and the produced glass was annealed at 280ºC for 2 hours.

In the second case after loading the charge into reactor the set-up was connected to the system of argon supply and the glass-forming melt was produced at pressure of 1 atmosphere under the same time-temperature modes.

In the third case the reagents were loaded from special ampoules. Before loading the system was evacuated down to the residual pressure of 10^{-5} Torr and heated at 500ºC for 5 hours for removal of water traces. Sulfur was distilled from ampoule 2 at 240ºC into reactor 7, then the ampoule was sealed off by A neck and mixture of germanium and antimony iodides was loaded at evaporator temperature of 160ºC. The system was sealed off by B, D necks and discharge tube 11 collapsed in burner flame. Then the reactor was placed into vertical furnace and the glass-forming melt was produced in the above-mentioned time-temperature modes. Should it be necessary, additional homogenization was carried out in the rocking furnace at 650^{0}C for 3 hours to increase homogeneity of the melt.

The prepared glasses were in the form of cylinders with diameter of 10 mm and length of 30–60 mm with glossy surface; their color was changing from dark red to orange depending upon composition.

Composition of the prepared samples was determined by the method of X-ray spectral micro-analysis (XRSA) using the scanning electron microscope SEM-515 (Philips, the Netherlands) equipped with energy dispersion analyzer EDAX-9900 (EDAX, the USA).

Vitreous nature of samples was proved by characteristic signal on DSC heating curves registered by differential scanning micro-calorimeter NETZSCH STA 409P (Germany).

Glasses were investigated by the methods of infra-red spectroscopy (IRS) by IR Fourier spectrometer IRP Prestige – 21 (Shimadzu, Japan) and of Raman scattering spectroscopy (RSS). The content of impurities was determined by the method of laser mass spectrometry (LMS) by laser mass analyzer Emal-2 (the Ukraine).

3. Results

Results on determination of glass compositions and on their thermal analysis are given in Table 1, where T_g^+ is the glass transition temperature determined with heating rate 10 K/min; T_w is the temperature corresponding to sample mass decrease by 1 mass %; ΔT is the difference of these temperatures.

Figs. 2 and 3 give the spectra of Raman scattering and of infrared transmission for glass samples in the range 20 – 700 cm^{-1} and 800 – 4000 cm^{-1}, respectively.

Table 2 gives the content of impurities in glass samples determined by LMS method.

Table 1. Composition and thermal properties of glasses

Sample	Composition, at.%				T_g^+, ºC	T_w, ºC	ΔT, ºC
	Ge	Sb	S	I			
No.1	24.7	7.9	60.6	6.9	259	420	161
No.2	21.5	9.2	64.1	5.3	271	475	204
No.3	22.4	7.5	61.1	8.9	251	388	137
No.4	20.8	7.9	60.2	11.1	232	>350	>118
No.5	26.1	–	64.6	9.3	302	>550	> 248

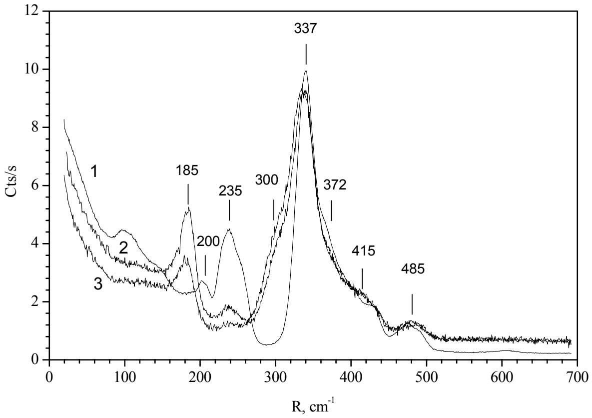

Fig.2. Raman scattering spectra for glasses with composition: 1 – sample No.1; 2 – sample No.2, 3 – sample No. 5.

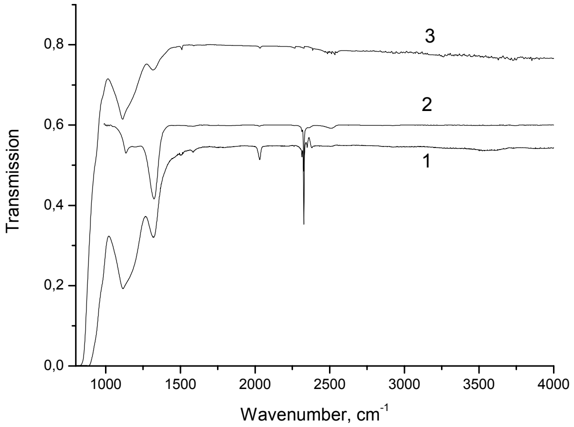

Fig.3. Transmission spectra of glasses: 1 – sample No.4, l = 26 mm, prepared in high-purity argon environment; 2 – sample No.2, l = 6.8 mm, prepared in the open system; 3 – sample No.5, l = 4.8 mm, prepared in vacuum.

Table 2. Content of impurities in glasses determined by LMS method.

Impurity	Content, ppm wt.	
	Sample No.3	Sample No.4
Si	1.8	0.8
Fe	0.3	< 0.07
K	0.5	< 0.1
Ca	0.5	< 0.1
Mg	< 0.05	< 0.05
Al	< 0.04	< 0.04
Ti	< 0.2	< 0.2
Co	< 0.2	< 0.2
Cr	< 0.1	< 0.1
Ni	< 0.1	< 0.1
Zn	< 0.3	< 0.3
Mn	< 0.1	< 0.1
Bi	< 1.0	< 0.4
V	< 0.5	< 0.1
Cu	< 0.2	< 0.2
Sn	< 1.3	< 0.1
W	< 2	< 2

4. Discussion

According to XRSA results the content of iodine in the prepared glasses is 5.3 – 11.1 at.% which proves a high-degree of conversion of germanium tetraiodide into germanium disulfide in the set-up equipped with mass transfer section. At the same time the deviation in the ratio of macro-components (Ge, Sb, S) in glasses with respect to that in the charge was 5 – 12% which is comparable with deviations in the traditional method used for preparation of chalcogenide glasses with purification of glass-forming melt by distillation.

A relatively low content of iodine in the prepared samples stipulates their sufficiently high glass transition temperatures (Table 2). Decrease in T_g^+, T_w and ΔT with the increase in iodine content is probably connected with its non-bridged position in glass network. Besides, according to [3] the substitution of sulfur for iodine in $GeS_{4/2}$ tetrahedra leads to the increase in content of free molecules S_8 dispersed in glass volume which decreases the general connection of structural network. The decrease of Sb content leads to increase of glass transition temperature (sample No. 5).

Analysis of the samples by RS method made it possible to determine the main structural fragments forming the glass network. Correlation of bands was carried out using the literature data on binary and ternary systems of similar composition [7–9]. The intensive band at 337 cm^{-1} corresponds to totally symmetrical vibrations of $GeS_{4/2}$ tetrahedra; the bands near 185, 200 and 235 cm^{-1} correspond to vibrations of the mixed GeS_xI_{4-x} tetrahedra (where $1 \leq x \leq 3$) and to Sb–Sb bonds in $S_2Sb–SbS_2$ units (180 cm^{-1}); the bands at 372 and 415 cm^{-1} refer to vibrations of binary tetrahedra $Ge_2S_4S_{2/2}$ and of two tetrahedra connected by bridge sulfur $S_3Ge – S – GeS_3$, respectively; the band at 300 cм$^{-1}$ refers to E mode of $SbS_{3/2}$ pyramids; superposition of bands near 485 cm^{-1} corresponds to symmetric vibrations of sulfur in –S – S – chains and S_8 rings.

In transmission spectra of glasses in 700 – 4000 cm^{-1} range the bands of selective impurity absorption are observed due to vibration of the bonds S – H (2510 cm^{-1}), C = S (1510 cm^{-1}), antisymmetric vibrations of the molecules CO_2 (2328 cm^{-1}) and COS (2032 cm^{-1}). Broad absorption bands in 700 – 1400 cm^{-1} range are probably the bands superposition corresponding to vibrations of Ge – O (1135 cm^{-1}), Sb – O (1120 cm^{-1}) bonds and to intrinsic vibrations of glass network – ν_3 of $GeS_{4/2}$ tetrahedra (1145 cm^{-1}), $SbS_{3/2}$ (≈1000 cm^{-1}) pyramids, S – S (1330 cm^{-1}) bond [8, 10, 11]. A sufficiently high content of oxygen impurity in the form of oxides is probably connected with partial hydrolysis of the iodides of germanium and antimony during interaction with moisture adsorbed upon reactor surface:

$$GeI_4 + 2H_2O \leftrightarrow GeO_2 + 4HI,$$
$$2SbI_3 + 3H_2O \leftrightarrow Sb_2O_3 + 6HI.$$

A sufficiently low content of hydrogen impurity in glasses in the form of SH-groups, calculated using the extinction coefficient of this impurity in As_2S_3 [12] glass, was $3\cdot10^{-5}$ mol % for sample No.4, and, perhaps, is due to interaction between germanium tetraiodide, antimony triiodide and molecular iodine with hydrogen sulfide leading to formation of hydrogen iodide

$$GeI_4 + 2H_2S \leftrightarrow GeS_2 + 4HI,$$
$$2SbI_3 + 3H_2S \leftrightarrow Sb_2S_3 + 6HI,$$
$$I_2 + H_2S \leftrightarrow S + 2HI,$$

which is removed from the glass-forming melt.

CO_2 impurity, observed in transmission spectra of samples No. 1, No. 2 and absent in the spectrum of sample No. 3, is, probably, enters the melt from environment. Holding of the glass-forming melt at 450–500°C in evacuated system or execution of synthesis in vacuum removes carbon dioxide dissolved in glass network.

According to LMS data the content of the most of transition metals in glasses does not exceed 0.1 ppm wt. A relatively low content of silicon (1–2 ppm wt) is due to the lowered temperatures of synthesis precluding the interaction of glass-forming melt with the walls of quartz apparatus. The content of silicon in the initial iodides without additional purification was 200 ppm wt. which, possibly, makes them the potential sources of this impurity in glass.

5. Conclusions

A technique for preparation of chalcoiodide glasses of Ge – Sb – S – I system with iodine content less than 5–11 at.% has been developed by interaction of germanium tetraiodide and antimony triiodide with sulfur melt at temperatures not exceeding 650°C. Removal of iodine from the glass-forming melt is a necessary condition for preparation of these glasses which is accomplished in the apparatus equipped with mass-transfer section. The prepared samples are characterized by low content of impurities of transition metals, silicon and hydrogen in the form of SH-groups.

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